A Project report

On

"Kinetics of Reaction of Benzyl Chloride with H_2S-Rich Aqueous Monoethanolamine Under Liquid-Liquid-Liquid Phase-Transfer Catalysis"

Submitted by

Nagarjun S

(Roll No. 211CH1037)

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Under the Guidance of

Dr. Sujit Sen

Department of Chemical Engineering

National Institute of Technology Rourkela

Rourkela-769008

Odisha

राष्ट्रीय प्रौद्योगिकी संस्थान राउरकेला

Natioanl Institute of Technology Rourkela

CERTIFICATE

This is to certify that the thesis entitled **"Kinetics of Reaction of Benzyl Chloride with H_2S-Rich Aqueous Monoethanolamine under Liquid-Liquid-Liquid Phase-Transfer Catalysis",** submitted by Nagarjun S to National Institute of Technology Rourkela, in fulfillment of the requirements of the degree of Master of Technology in Chemical Engineering is a bonafide record of the research work carried out by him, in the Department of Chemical Engineering, National Institute of Technology, Rourkela under my supervision and guidance. Mr. Srinivas has worked on this topic from July, 2012 until April, 2013 and the thesis, in my opinion, is worthy of consideration for the award of the degree of "Master of Technology" in accordance with the regulations of this Institute. The results embodied in the thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

Date: 24th May, 2013

Dr. Sujit Sen
Department of Chemical Engineering
National Institute of Technology
Rourkela-769008

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S.Nagarjun (211ch1037)
Master of Technology
Dept of Chemical Engg.,
NIT Rourkela

LIST OF ABBREVIATIONS

BC	Benzyl Chloride
BM	Benzyl Mercaptan
DBS	DiBenzyl Sulfide
GLC	Gas Liquid Chromatography
MDEA	Monodiethanolamine
MEA	Monoethanolamine
OVAT	One Variable at a time
PEG	Polyethylene Glycol
PTC	Phase transfer catalysis
TBAB	Tetrabutyl Ammonium Bromide

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ABSTRACT

This thesis work engages the study of treatment of hydrogen sulphide gas based on phase transfer catalysis for the production of DiBenzyl Sulphide and other organic sulphides at room temperature and optimizing the conditions for 100% selectivity and maximum conversion. This study focuses on the condition optimization for preparation of Dibenzyl sulphide and also maximum absorption of H_2S on cheaper solvents. Benzyl chloride was used as the reactant and MethylEthylAmine (MEA) for absorption of H_2S gas. Phase transfer catalyst chosen was PEG-400 for its non-pollutant nature and cost of course. Toluene was made the organic Solvent. The amount of catalyst required was around 0.12wt% because of its low reactivity. The optimum time was around 7-8 hrs and the sulphide concentration for DBS formation was 1.646 kmol/m^3 at a temperature of 60ºC. The experiments were done using one variable at a time approach as it was a simple system.

Keywords: Hydrogen sulfide; dibenzyl sulfide; Monoethanol amine; phase transfer catalyst; selectivity; optimization

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CHAPTER 1

INTRODUCTION

Abstract

This chapter describes an overview of the present research and its importance. It includes introduction to concept and different types of PTC, organosulfur compounds and preparation methods, importance of its removal and recovery, environmental problems and treatment methods of H_2S, Solvents and catalysts used in the process, mechanism of tri-liquid PTC, the objectives of this study and a note on the structure and organization of the thesis.

1. INTRODUCTION

The phase transfer catalysis (PTC) is very popular for the past 4 decades since the term was introduced by stark in 1971 to explain the critical role of tetraalkylammonium or phosphonium salts (Q^+X^-) in the reactions between two substances located in different immiscible phases. Even though it was introduced in early 70's, PTC is an important process without which humans cannot survive. There are some phase transfer agents in human body like choline and phenacron which are quaternary ammonium salts and responsible for important processes like structural integrity, signalling roles for cell membranes and most importantly to accelerate the absorbtion and utilization of oxygen by human cells.

1.1. CONCEPT AND ADVANTAGES OF PTC

The concept of phase transfer catalysis is using a catalyst which facilitates the migration of a reactant in a heterogeneous system from one phase into another phase where reaction can take place. It also enhances the reaction rate of an organic-water system by addition of a catalyst which alters the rate of transfer of water-soluble reactant across the interface to the organic phase. The first industrial usage of PTC reaction is shown below (Ind. Chem. Chem., 1946, 38, 207).

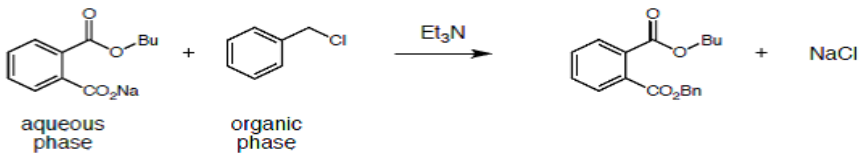


Figure 1.First clear-cut example of the commercial use of PTC

It posses lot of advantages as it is a form of green chemistry. Some to be listed are

- Elimination of organic solvents

- Use of simple and inexpensive reagents (NaOH, KOH, K_2CO_3 instead of NaH, KHMDS t-BuOK, etc.)
- High yields and purity of products
- Simplicity and highly scalable
- Low energy consumption and low investment cost

1.2. CLASSIFICATION OF PTC REACTIONS

PTC reactions can be classified into two types: soluble PTC and insoluble PTC. Each type can be further divided into several categories.

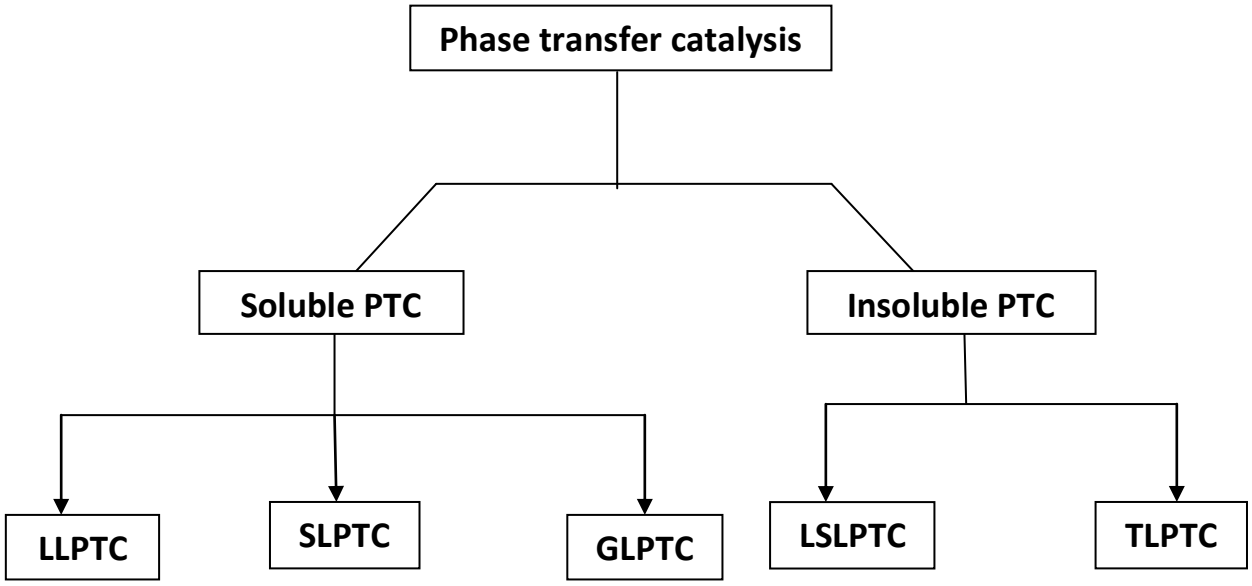


Figure 2: Classification of PTC Reactions

Insoluble PTC consists of liquid–solid–liquid PTC (LSLPTC) and tri-liquid PTC (TLPTC), by which the catalyst can be recovered and reused, showing the great potential in large-scale production for industry. The catalyst used in LSLPTC is immobilized on an organic or inorganic support, while in TLPTC it is concentrated within a viscous layer located between the organic and aqueous phases. Soluble PTC includes liquid–liquid PTC (LLPTC), solid–liquid PTC (SLPTC) and gas–liquid PTC (GLPTC). There are also non-typical PTC reactions termed inverse PTC (IPTC) and reverse PTC (RPTC), and these are different in catalyst type and transfer route, compared to normal PTC.

1.3. ORGANOSULFUR COMPOUNDS

Organosulfur compounds which finds applications in many places like petroleum industries, corrosion inhibition has been dealt with here. There are 13 different types of such compounds which are listed below. Two of these compounds which have high industrial importance form the basis of our work.

- Thiols like Methanethiol – CH_3SH, 1-Propanethiol – C_3H_7SH ,2-Propanethiol – $CH_3CH(SH)CH_3$, tert-Butyl mercaptan – $C(CH_3)_3SH$, Thiophenol - C_6H_5SH, Dimercaptosuccinic acid and thioacetic acid.
- Disulfides, polysulfides like Dibenzylsulfide, DibenzylDisulfide, thioanisole, etc
- Thioethers, thioesters, thioacetals
- Sulfoxides, sulfones and thiosulfinates
- Sulfimides, sulfoximides, sulfonediimines
- S-Nitrosothiols
- Sulfur halides
- Thioketones, thioaldehydes, and related compounds
- Thiocarboxylic acids and thioamides
- Sulfonic, sulfinic andsulfenic acids, esters, amides and related compounds
- Sulfonium, oxosulfonium and related salts
- Sulfonium, oxosulfonium and thiocarbonylylides
- Sulfuranes and persulfuranes

1.3.1. PREPARATION METHODS

There are lot of preparation methods of organic sulphides from time immemorial. Here are some of the methods which were surpassed by PTC with its advantages.

According to Tassinaria, symmetrical organic sulfides are formed when a cold carbon disulfide solution of a phenol is treated with sulphur dichloride. The general method adopted

for the preparation of the compounds is proportionate amount of phenol which is dissolved in hydrochloric acid and a white or yellow precipitate separates. This precipitate is filtered off, and is recrystallized from benzene. White crystals of the desired sulfide are thereby obtained.

The reaction of alkyl bromides or iodides with sodium sulfide to give organic sulfides is well known. This research activity required a sample of bis-(Zethylhexyl) sulfide. The reaction of 2-ethyl hexyl chloride with sodium sulfide was inviting in suitable conditions. This reaction was very slow inaqueous or alcoholic solution. The use of ethylene glycol as solvent gave a much more satisfactory procedure. The yield of bis-(2-ethylhexyl) sulfide from such a run was 76%. The usefulness of ethylene glycol as a solvent in the reaction of an organic chloride with sodium sulfide, was carried out employing 1,4-dichlorobutane. This reaction gave a 67% yield of tetramethylene sulfide.

To synthesize Arylethynyl sulfides and bis(arylethynyl) sulfide a one-pot, three-step strategy that starts from arylethanonyl sulfides and bis(arylethanonyl) sulphides was developed by adding lithium hexamethyldisilazane (LHMDS), $ClP(O)(OEt)_2$, and LHMDS to a tetrahydrofuran solution of different substrates [arylethanonyl sulfides or bis(arylethanonyl) sulphides. The reaction procedure involved the formation of an enol phosphate and a subsequent base-induced elimination.

And another procedure which involved a reaction of disulfides with suitable alkyl or aryl halides which is promoted by commercial zinc powder in the presence of $AlCl_3$ in aqueous media at 65°C has been one of the recent preparation methods.

They can be synthesized by several procedures, including reaction of an alkyl halide (RX, where X is a halogen) with the sulfur reagent thiourea, $(NH_2)_2C=S$, or with thiocyanate salts; reaction of organomagnesium (RMgX) or organolithium (RLiX) compounds with elemental sulfur; or addition of hydrogen sulfide or thioacetic acid ($CH_3C(O)SH$) to alkenes.

A number of examples of synthesis of sulfides were described above in all reactions. A unique synthesis of sulfides is explained here by reacting ethylene with sulfur dichloride to form bis(β-chloroethyl) sulfide, known as sulfur mustard, or mustard gas, a blister-forming chemical warfare agent. This reaction has been applied to the synthesis of cyclic and bi-cyclic dichlorosulfides as well.

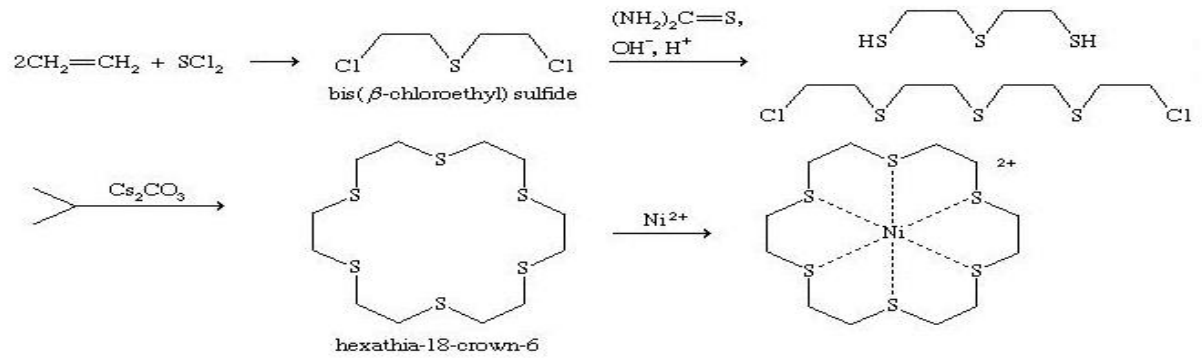


Figure 3: Preparation methods of sulfides from ethylene

1.4. H_2S, ENVIRONMENTAL PROBLEMS & SOLUTIONS

All the acidic gases exhaust are harmful to human beings and the level of release which would cause harm is the thing which is to be noted to decide the harmfulness of those gases. In that way H_2S is one of the very poisonous gases which can be harmful at low ppm levels. It is heavier than air and its mixture with air becomes an explosive. So it has to be definitely treated before released into the atmosphere. Even when not released into the atmosphere, it causes other problems like corrosion of process equipment, deterioration and deactivation of the catalysts, undesired side reactions, increase in the process pressure requirements and increase in the gas compressor capacity (Hamblin, 1973). Because of its colorless nature, it's hard to detect its presence unless it causes any harm. The gas is released whenever elemental sulfur comes in contact with organic material that is why it is found more in petroleum industries where sulfur reacts with the hydrocarbons at a large amount. So we would be concentrating on this industry for the main raw material hydrogen sulfide. First let us have an overview of the methods available for its treatment.

Claus process remained the favorite of industries for many decades until the alkanolamine process overtook it in the recent times because of its ease of operation and reduced energy usage, but still there has been a lot of developments made for the former one.

Superclaus: A special catalyst in the last reactor oxidizes the H_2S selectively to sulfur, avoiding formation of SO_2. Significantly higher conversions are obtained at modest cost.

Oxygen Claus: The combustion air is mixed with pure oxygen. This reduces the amount of nitrogen passing through the unit, making it possible to increase throughput.

Better Catalysts: Higher activities have been achieved with catalysts that provide higher surface areas and macroporosity.

These are the improvements going on with the Claus which led to the crsytasulf and LO-CAT processes. But none of the processes is helpful is removing the hydrogen from it which would be of great economical importance, it is helpful the separating the elemental sulphur. But this gas can be used for the synthesizing of above mentioned organosulfur compounds when used with specific reactants which would be more economical compared to any other process and also less energy requirement. So this process would be of coalesce use because of its ability to treat environmental problems and synthesize fine chemicals.

1.4.1. ALKANOLAMINE BASED PROCESS

The alkanolamine based process achieves the de-acidification of feed gas by chemical absorption with an aqueous solution of Methyl-DiEthanol-Amine (MDEA) or DEA or MEA. Alkanolamine is used at high concentration without addition of a corrosion inhibitor. It is based on total's operation experience of corrosion control with such units.

The very fast reaction between H_2S and MEA provides the base for this process to be commercially achievable. For a good understanding of the process, the reaction mechanisms of H_2S with MEA is presented below:

H_2S reacts with the amine to give an amine hydrosulphide:

$$H_2S + R_3N \longrightarrow HS^- , R_3NH^+$$

As regards to the kinetics, rate of reaction (1) is infinite. This process can also be used for CO_2 removal. The difference in reaction rates between H_2S and CO_2 is the basis of the selective absorption. The MEA was chosen for the work, here we would discuss the advantages and disadvantages of it to get a clear picture of what the alkanolamine can provide us to make the process feasible.

1.5. SOLVENTS

1.5.1. MONOETHANOLAMINE (MW=61)

Advantages

- The low molecular weight of MEA results in high solution capacity at moderate concentrations (on weight basis).
- Most reactive
- Relative ease with which it can be reclaimed from the contaminated solution

Disadvantages

- Being most reactive forms irreversible products with CO_2 and CS_2, not suitable for gases having high amount of those
- High heat of reaction with H_2S(820 BTU/lb) and CO_2(825 BTU/lb) leads to higher energy requirements for stripping
- Significant vaporization losses due to high vapour pressure

Uses

MEA in solutions, acting as a weak base, neutralizes acidic compounds dissolved in the solution to turn the molecules into an ionic form, making them polar and considerably more soluble in a cold MEA solution. MEA is not only used as feedstock in the production of detergents, but also as emulsifiers, polishes, pharmaceuticals, corrosion inhibitors and chemical intermediates.

1.5.2. TOLUENE

Toluene, formerly known as toluol is a clear, water-insoluble liquid with the typical smell of paint thinners. It is a mono-substituted benzene derivative in which a single hydrogen atom from a group of six atoms from the benzene molecule has been replaced by a univalent group, in this case CH_3. Its molar mass is 92 g/mol and density is 0.87 g/mL. The other physical

properties which are important to us are boiling point and solubility which is 111°C and 0.47 g/L in water

Advantages

- Relatively inexpensive, readily available in any quantity and purity
- Not a listed carcinogen
- The methyl group makes it around 25 times more reactive than benzene
- Vapour pressure of toluene is less, hence changes in concentration due to evaportaion during the experiment are not as significant.
- Freezing point of toluene (-94.99 OC) is also much lower and this enables low temperature studies

Disadvantages

- Often not a really good solvent comparatively
- A VOC and has a fairly low exposure limit

Uses

Industrial uses of toluene include dealkylation to benzene, and the disproportionation to a mixture of benzene and xylene. When oxidized it yields benzaldehyde and benzoic acid, two important intermediates in chemistry. It is also used as a carbon source for making Multi-Wall Carbon Nanotubes. Toluene is another in a group of fuels that have recently been used as components for jet fuel surrogate blends. Toluene has also been used as a coolant for its good heat transfer capabilities and also been used in the process of removing the cocaine from coca leaves in the production of Coca-Cola syrup.

1.6. PRESENT WORK

The focus of research in this direction has been to develop low cost and environmentally benign alternatives to the Claus process. Other alternative technologies have been developed for the removal of H_2S, but there has been very less studies on the usage of those acidic gases to be utilized for the synthesis of fine value added chemicals. The chemicals DBS(dibenzylsulfide) and BM(benzyl mercaptan) have been synthesized using different ways like reduction of disulfide using zinc powder in the presence of $AlCl_3$ or deoxygenation of sulfoxide and BM was synthesized from BC was also

reported in the literature using various types of reagents such as methanolic ammonium hydrosulfide (NH_4SH), aqueous ammonium hydrosulphide, sodium hydrosulfidesalt under hydrogen sulfide atmosphere and polymer-supported hydrosulphide.

1.6.1. APPLICATION OF PTC

As mentioned above the acidic gases are to be used for synthesis of fine chemicals like dibenzyl sulphide and benzyl mercaptan. Since mono ethanol amine and benzyl chloride are two different phases, their reaction is very difficult and even if it happens the yield is below 40% and the reaction rate is very slow. So phase transfer catalyst can be used for this purpose of reacting two different phases. This method has been used for nearly 4 decades and therefore many catalysts are available.

1.6.2. TYPES OF CATALYST AND COMPARISON

PEG'S are the cheapest while crown ethers and cryptands are the most expensive of the commonly used PT catalysts. Crown ethers and cryptands, besides their high costs, are also toxic, and are to be avoided whenever possible. Quaternary ammonium salts are usually useful in neutral or acidic media up to 100-150'C. Dequaternization of the quaternary onium salt by the reverse Menshutkin reaction occurs at elevated temperatures in non-basic media. PEG'S, crown ethers, and cryptands are more stable at higher temperatures and can be used up to temperatures of 150-200ºC. However, it should be noted that many applications of PTC require temperatures of 50-120ºC and quaternary onium salts are highly active, stable, and widely applicable under these conditions. Crown ether, cryptands, and PEG'S also show higher stability to basic conditions than quaternary onium salts. In the presence of bases like 50% NaOH, quatemary ammonium salts decompose by Hofmann elimination

Table 1. Comparison of Catalysts and its Cost

Catalyst	Cost	Stability and Activity	Use and recovery of Catalyst
Ammonium Salts	Cheap	Moderately stable under basic conditions and upto 100 C. Moderately active	Widely used. Recovery is relatively difficult
Phosphonium Salts	Costlier than ammonium salts	More stable thermally than ammonium, although less stable under basic condition	Widely used. Recovery is relatively difficult

Crown ethers	Expensive	Stable and highly active both under basic conditions and higher temp upto 50-200 C	Often used. Recovery is difficult and poses environmental issue due to their toxicity
Cryptands	Expensive	Stable and highly reactive except in presence of strong acids	Used sometimes despite high cost and toxicity due to higher reactivity
PEG	Very cheap	More stable than quarternary ammonium salts, but less reactive	Often used. Can be used when larger quantities of catalysts cause no problems. Relatively easy to recover

[Sanjeev D. Naik and L. K. Doraiswamy]

PEG's are good alternatives to onium salts as cheap and stable PT catalysts inreactions in basic media and at elevated temperatures. However, in comparison to crown ethers, cryptands, and oniumsalts, larger quantities of PEG are required due to their comparatively lower activity, but there is no loss as recovery via distillation is easily accomplished.

1.6.3. PEG-THE BEST CATALYST KNOWN

Once all the other parameters of a process being finalized, the last economical factor considered would be the cost of catalyst and it is confirmed from the above table, PEG is the cheapest catalyst available. Other than these there are lot other properties which take them to the top of the table when considered for a phase transfer reaction.

It's called the poor chemists crown as its activity is very similar to crown ethers, sometimes even better than it and far cheaper to it. Another highlighting factor that comes into play is the environmental degradability, PEG's are non-toxic and easily biodegradable. With environmental factors being the primary concern these days, it can be more effective than other catalyst available. For reactions involving hydroxide transfer in solid-liquid systems in moderately polar organic solvents, PEG's are very good PT catalysts with activities better than those of crown ethers. Solubility in water makes them poor catalysts for liquid-liquid systems, but in our case the PEG forms a third catalyst-rich phase and functions as an active PT catalyst.

PEG's being polymers are stable at high temperatures. It can still be active above 100°C and can operate up to 150°C, but depends on the weight of the PEG. High MW polymers are more stable. Even it can withstand basic conditions and does not get deactivated in high pH.

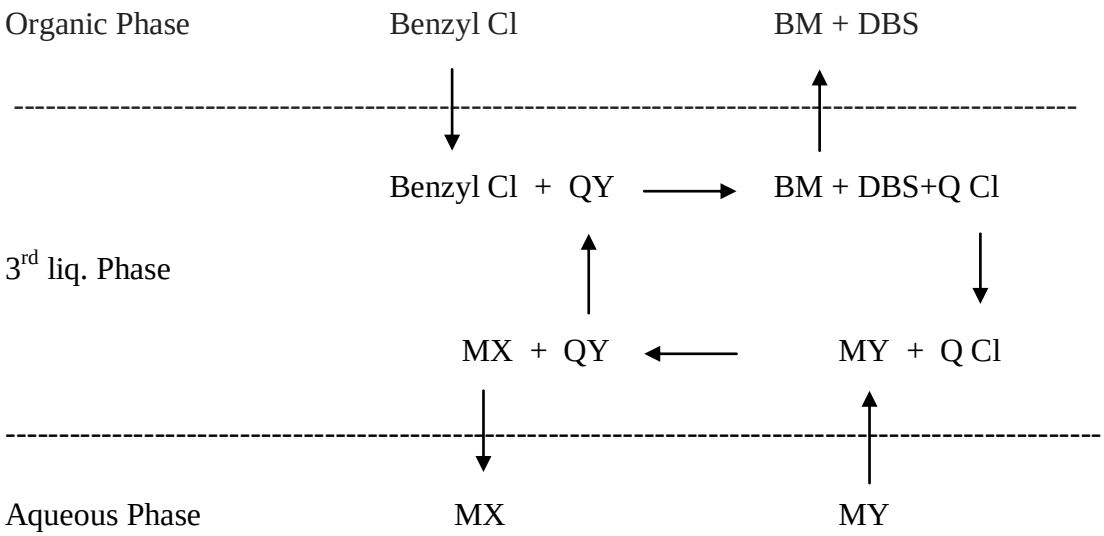
With the new era turning towards multiphase catalysts, again PEG can be the most promising catalyst because of its ability to act as polymer support, already there have been hundreds of literature in this area. Even when it's not in a multiphase catalyst system, the other positives of PEG, where no organic or any other hazardous solvent need not be used makes it more attractive.

Considering the effects of other things affecting the phase transfer reaction which will be discussed later, PEG also the qualities of a surfactant which increases the ability of cations and anions for transfer and thus fastening the reaction rate.

1.7. MECHANISM OF TRILIQUID PTC

Neumann and Sasson et al. investigated the isomerization of allylanisole using PEG as the catalyst in a toluene and aqueous KOH solution. They observed that a third-liquid phase was formed between the aqueous and the organic phases. This was the first report regarding tri-liquid PTC. In this instance the catalyst was found to be concentrated within a viscous liquid phase that was insoluble in both aqueous and organic phases because of the density difference. The third-liquid phase generally contains little of the organic and aqueous reactants, but mainly the highly concentrated catalyst, which exhibited hydrophilic and lipophilic properties. Polarity of the solvents and amount of salts can greatly affect the solubility of catalyst in the organic phase leading to such a formation. There were examples of methanol reducing the solubility of PEG and salts like NaOH reducing the solubility of ammonium and phosphonium salts.

The catalyst doesn't stay 100% in the third phase, trace amounts of it are found in organic and aqueous phases too, but we would concentrating on the mechanism of tri-liquid phase, as other two comes under general PTC.



The reaction occurs in at least two steps

- Step 1: The intrinsic reaction or organic-phase displacement reaction step
- Step 2: The transfer step

–If this step is rate determining **Extraction Mechanism**

–If this step is rate determining **Interfacial Mechanism**

The following reaction is considered for good understanding of these two steps

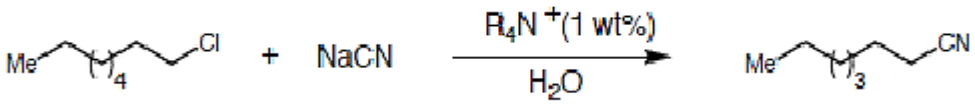


Figure 4. 1-chlorooctane and sodium cyanide solution in presence of phase transfer catalyst

1.7.1. INTRINSIC STEP

Once in solution the anion must be sufficiently reactive to allow displacement to proceed. The poor reactivity is due to the tight ion pairs of anion present here or large interaction energy binding the two ions together.

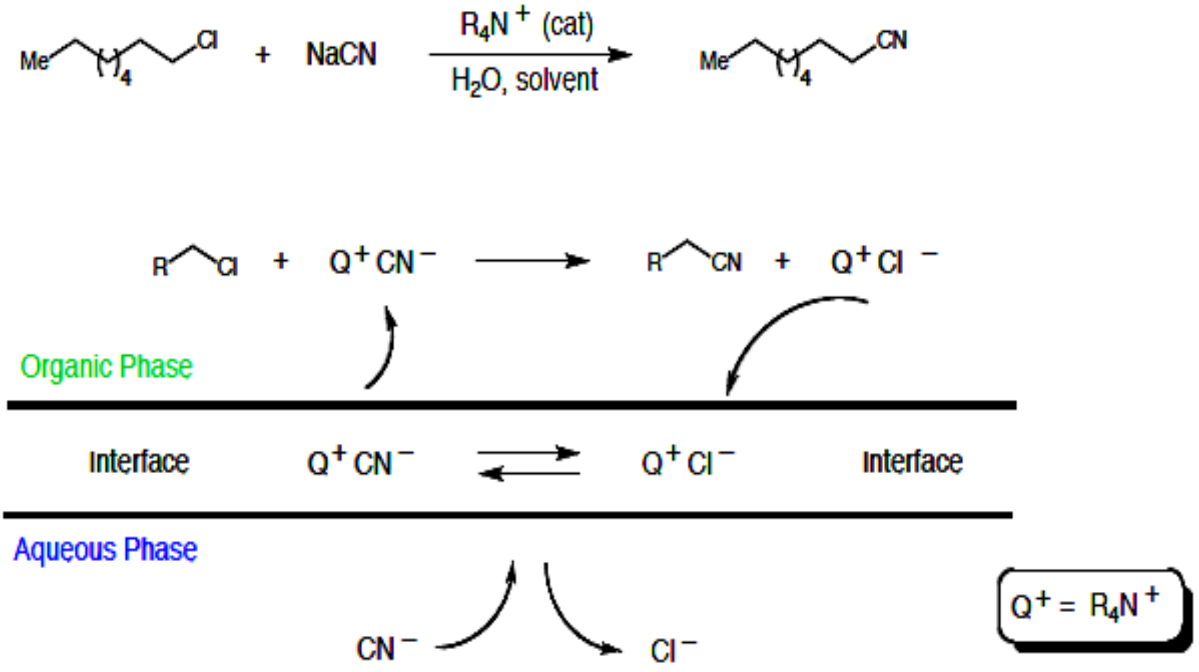


Figure 5. Intrinsic step of reaction in figure 4

The difference in ionic radii can be translated into ionic interaction energies by simple coulombic calculations. If these differences in ion-pair energies are translated in reduction of kinetic activation energies then a 5 Kcal/mol difference in activation energy is equivalent to a 4400-fold changes in reaction rate.

1.7.2. Transfer step

There are two general mechanisms for the step as proposed by stark and maskoza and both are correct depending on the catalyst used. The figure on the right represents the mechanism for small and medium sized quartenary cations and the second goes correct with medium to large sized cations. For asymmetric PTC, most catalyst employed remains in the organic phase with transfer occurring at the interface.

But there is a difference when the catalyst are polymers or crown ethers other than quarternary ammonium or phosphonium salts, ionic liquids, etc. and this is called as liquid-liquid-liquid(L-L-L) mechanism when the catalyst is a liquid like low weight polymers and liquid-solid-liquid when catalyst is a solid like heavy polymers.

This overcomes the disadvantages of catalyst wastage in liquid-liquid mechanism and low reactivity in solid-liquid mechanism.

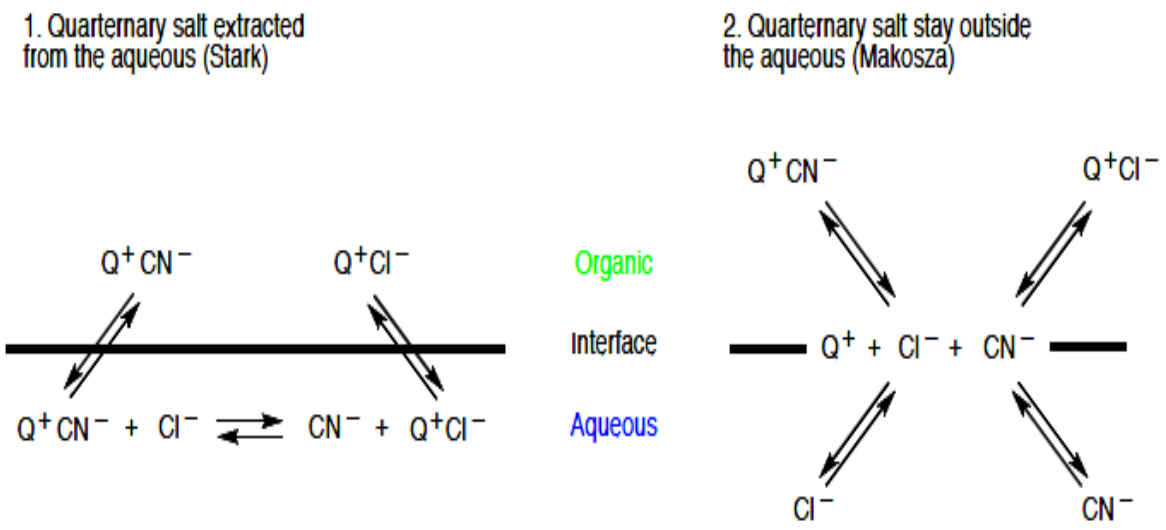


Figure 6. Transfer steps of PTC reaction

1.7.3. Factors governing the transfer step

(i) Interfacial area

-Interfacial tension: More interfacial tension result in a decrease of the interfacial area. Highly non-polar solvents and highly concentrated aqueous solution have the highest interfacial tension

-Presence of surfactants: Surfactants increase the interfacial area by helping the formation of tiny droplets

-Stirring: At low stirring rates the interfacial area varies with the square of the stirrer speed(agitation energy =mass x velocity2). The use of ultrasound can yield high levels of agitation

(ii) The nature of the anion:

-Large weakly-hydrated or organic anions such as perchlorate, iodide and phenolate are easily transferred while small hydrated anions such as fluorides or hydroxide are poorly transferred

(iii) Bulkiness of the quaternary cation catalyst

-As alkyl groups becomes larger and larger the rate of transfer becomes slower and slower

-The use of unsymmetrical quaternary cations much closer approach of the cationic center to the interface

-Catalyst's bulkiness also reduces transfer rates by lowering the maximum possible concentration at the interface.

1.7.4. Selection of appropriate reaction conditions using PTC matrix

Understanding and prediction of PTC reaction systems requires some knowledge of both the rates of transfer and the rates of the intrinsic organic-phase reaction. For new systems it is necessary to make some guesses and extrapolations from known systems

Table 2: Effect of variables on intrinsic reaction and transfer rate

Variable	**Effect on transfer step**	**Effect on intrinsic reaction step**
Catalyst structure	+++	+++
Agitation	++++	-
Type of inorganic anion	++++	++++
Water concentration	++	+
Organic solvent	+	++
Temperature	+	+++
Cocatalyst	++	+++
Organic reactant structure	-	++++

1.7.5. PTC Matrix

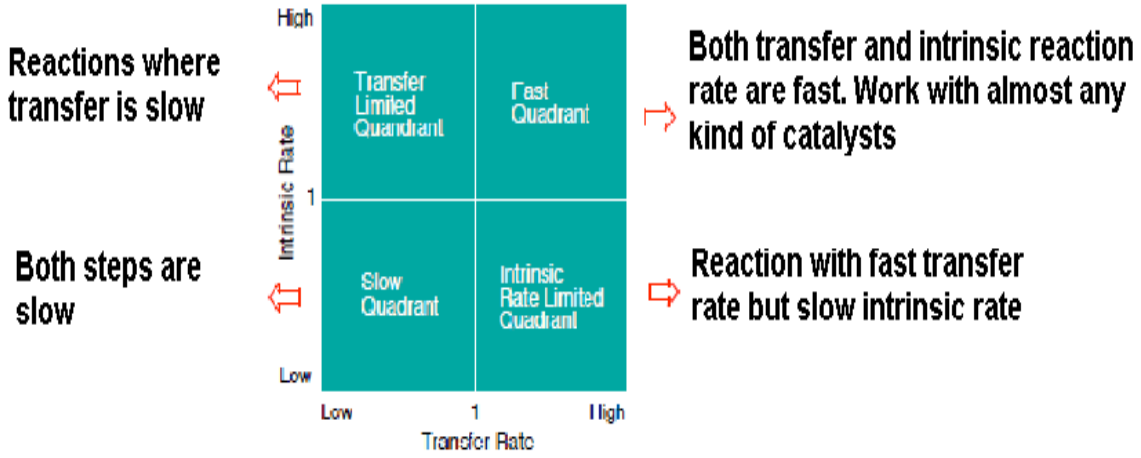


Figure 7. Matrix of PTC reaction showing reaction rates

1.7.6. Effect of PTC variables

1. Agitation (Influence only the transfer rate)

– Agitation speed should be high enough so that it has no influence on the overall reaction rate

2. Concentration of H_2O

– With anions difficult to transfer having saturated aqueous solution drives the equilibrium towards the catalyst substrate complex. Also, minimal amounts of water reduces the hydration of ions

3. Organic solvents

– Affect the interfacial tension which influences the transfer rate

4. Temperature

– Most quaternary ammonium salts decomposes at higher temperature, for examples 50-70 ºC for systems containing KOH

– CH_2Cl_2 is used extensively because of it dissolves most quaternary salts and is also hydrophobic

– For asymmetric PTC non-polar solvents such as toluene are used extensively because they maximize the interactions between the two counter ions.

5. Co-catalyst

– Often used to help one of the two steps. For example, addition of alcohols, particularly diols, significantly increase the ease of hydroxide anion transfer

6. Catalyst

– The size and shape affect the anion activation

– Ability to solubilize the aqueous phase reagent into the organic phase Transfer rate

– Bulkiness can slow the transfer rate

– The stability of the catalyst under the reaction conditions

– The surfactant property of the catalyst Transfer rate

Different reactions respond to these characteristics in different ways, thus not one catalyst structure is best for all reactions.

CHAPTER 2

LITERATURE SURVEY

Abstract

This chapter deals with the literature review related to the use of alkanolamine as acid gas absorbent, different methods of preparation of aromatic sulfides and mercaptans and the usage of PEG in various systems.

2.1 Use of Ammonium Hydroxide and Aqueous Alkanolamines for Removal of H_2S

The removal and recovery of hydrogen sulfide (H_2S) from the gas streams by ammonium hydroxide are well documented **(Kohl and Nielsen, 1997)**. Process was also developed (Hamblin, 1973) for removal of H2S from gas streams using ammonium hydroxide to produce ammonium hydrosulfide, which was further oxidized by an air stream to get an effluent stream containing ammonium polysulfide and treating the ammonium polysulfide containing stream to recover elemental sulfur. Recently, **Asai et al. (1989)** studied the rates of simultaneous absorption of H_2S and ammonia into water in an agitated vessel with a flat interface and **Rumpf et al. (1999)** studied the simultaneous solubility of ammonia and hydrogen sulfide in water at temperatures from 313 to 393 K and total pressures up to 0.7 MPa.

On the other hand, aqueous alkanolamines are now-a-days widely used in industry for the removal of H_2S from gas streams as discussed in Chapter 1. Lot of research works are also devoted to the study on the equilibrium solubility of pure H_2S, mixture of acid gases (H_2S and CO_2), and the mathematical representation of the experimental solubility data for H_2S, CO_2 and their mixture using various alkanolamines **(Austgen et al., 1989; Weiland et al., 1993; Kaewsichan et al., 2001; Al-Baghli et al., 2001; Sidi-Boumedine et al., 2004).**

2.2 Preparation of Benzyl Mercaptan

Benzyl Mercaptan (BM) is useful as a raw material for the synthesis of herbicides in the thiocarbamate family (Labat, 1989). Preparation of BM from benzyl chloride using sodium hydrosulfide and ammonium hydrosulfide reagents is well documented.

As for example, **Hoffman and Reid (1923)** prepared BM by reacting benzyl chloride with ethanolic solution of molten sodium sulfide (melted at 90°C) saturated with hydrogen sulfide (H_2S). The mixture was allowed to stand in the cold, with frequent shaking for 4 days. This shows the importance of phase transfer catalyst without which a reaction can take up to 4 days with less yield.

Heather (1988) prepared BM by a similar reaction in which benzyl chloride was reacted with sodium hydrosulfide in the two-phase conditions under H_2S atmosphere at a temperature of about 50°C (stirred for approximately 5 hours), then temperature was raised to about 80°C for the balance of the reaction (stirred for an additional 1.5 hours). High temperatures and 7 hrs were the required which are the constraints for this process.

Bittell and Speier (1978) prepared BM in a continuous process which can be useful for commercialization by using a solution of NH_3 and methanol saturated with H_2S at 0°C. Benzyl chloride was added to this methanolic ammonium hydrosulfide (NH_4SH) solution at 0°C while slowly bubbling H_2S through the solution. The reaction was completed in 1 h with BM (92%) and DBS (8%) as the detectable products. But maintaining such a low temperature is another commercial barrier.

BM was also prepared from the corresponding thioacetates via Pd-catalyzed methanolysis with borohydride exchange resin (Choi and Yoon, 1995a) and from the corresponding alkyl halides and epoxides using hydrosulfide exchange resin in methanol in the presence of equimolar amounts of triethylammonium chloride (Choi and Yoon, 1995b).

2.3. Preparation of Benzyl chloride

Dibenzyl sulfide (DBS) finds many applications such as additives for extreme pressure lubricants, anti-wear additives for motor oils, stabilizers for photographic emulsions, in refining and recovery of precious metals, and in different anticorrosive formulations (Pradhan and Sharma, 1990).

Pradhan and Sharma (1990) showed the usage of PTC to synthesize DBS and bis (*p*-chlorobenzyl) sulfide by reacting the respective chlorides with sodium sulfide using different phase transfer catalysts (PTC) under liquid-liquid and solid-liquid mode. Tetrabutylammonium bromide (TBAB) was found to be the most effective out of the six catalysts they tried under solid liquid mode of operation. This is the study which showed TBAB as one the best catalyst but recovery of the catalyst was an barricade to take the process further.

The kinetic study was also done by **Pradhan and Sharma (1992a)** for the same system (i.e., preparation of DBS and bis (4-chlorobenzyl) sulfide under solid-liquid modes with solid sodium sulfide) using easily separable non-impregnated inorganic solid catalyst like basic

alumina and Amberlyt A27 (Cl- form) anion exchange resins which introduced resins also into the one of the best useful catalyst.

2.4. Use of PEG and study of third liquid phase

Ido et al (1999) investigate how the property of third phase affects the reaction rate in a phase transfer catalytic reaction system. It showed the effect of salts in the aqueous phase, but it was **Der-her wang et al (1994)** who gave a detailed description on the solvent and salt effects on the third liquid phase once it came into practice around 1990. The effects of solvents and salts (including base) on the formation of a third liquid phase, distribution of catalyst, reaction mechanism and reaction rate in the reaction between n-butyl bromide and sodium phenolate (NaOPh) with tetrabutylammonium bromide (QBr) as a phase transfer catalyst were investigated. The organic solvents used include chlorobenzene, toluene and hexane while sodium bromide and sodium hydroxide were tested in the study of salt effects. It is found that salts can force QBr (or QOH) out from the aqueous phase to the organic phase or to form a third liquid phase depending on the organic solvent. So the type of solvent (polarity) and the amount of salts played major role.

Jin et al (2001) investigated third phase when PEG was used as because of the polymer properties it varies from other phase transfer catalysts. The production rate at the three-phase system is higher by seven times than that at the two-phase system. The ether production rate and its selectivity are dependent on the initial concentration of *n*-butanol. These are affected by the properties of the third phase, especially the concentrations of *n*-butanol and water in the third phase.

PEG 400 has been one of the promising catalysts when it comes to triphase, it has grafted into other polymer wall like polystyrene and in cinchona and each time the reaction rates has went up dramatically. Yadav et al (2012) studied the process intensification and waste minimization while using PEG as catalyst for the preparation of mandelic acid. And there has been various other recent places of using PEG from basic to complex reactions. (**Zhing Li et al (2002), Gong jin (2004), Nishtad et al(2008), Nana V.Shitole (2012)**)

The PEG has some other excellent properties such as surfactant that too in the developing fields such as synthesis of nanoparticles. Ching-An peng(2001) investigated the usage of PEG as surfactants for perflourocarbon emulsions which can be injected into human being without any side effects because of its biodegradability and phatacytosis resistant.

Other than this for preparation of metal nanorods like zinc and copper PEG has been used as the surfactant. Less-populated and well-isolated ZnO nanorods were prepared from a simple solution method by using polyethylene glycol (PEG) surfactant molecules. The structural and morphological information provided by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM) demonstrated the high purity of the ZnO nanorods that were free from any unknown impurities (**Seung et al (2008), Nishtar et al (2008)**). The products produced were of high purity, so it implies not the need for surfactants in our system for reduction of interfacial tension during transfer.

CHAPTER 3

EXPERIMENTAL

Abstract

This chapter deals with the detailed experimental procedure followed in every step of the experimental studies. It includes chemicals, equipment details, preparation of several reagents, experimental method and analytical procedure.

3.1. Chemicals

Preparation of H_2S rich mono ethanol amine

- Sulphuric acid from Merck Pvt. Ltd., Mumbai (98%)
- Iron Sulphide fused sticks for producing H_2S from Merck Pvt. Ltd., Mumbai
- Silicon high vacuum grease from RFCL Limited, New Delhi
- Mono ethanolamine from Loba Chemie Pvt. Ltd., Mumbai (99%)

Estimation of sulphide content

- Sodium thiosulphatepentahydrate (purified) from Merck Pvt. Ltd. (≥99%)
- Potassium iodate GR from Merck Pvt. Ltd. (≥99.5%)
- Sodium hydroxide pellets (purified) from Merck Pvt. Ltd. (≥97%)
- Starch soluble GR from Merck Pvt. Ltd.
- Potassium iodide GR from Merck Pvt. Ltd. (99.8%)

Preparation of Organic Phase

- Toluene from RFCL Limited, New Delhi (≥99.5%)
- Benzyl Chloride from Merck (India) Ltd., Mumbai (≥99%)
- Acetone from RFCL Limited, New Delhi (99.5%)

Catalyst

- PEG-400 from Merck Pvt. Ltd., Mumbai

3.2. Preparation of H_2S rich MEA

Preparation of this solution is done simultaneously with the production of H_2S gas from the kipp's apparatus which is an apparatus for the preparation of the small volume of gases. It consists of 3 stacked cylinders where it is filled with different reactants which is in our case Iron(II) Sulfide and Hydrochloric acid. The middle cylinder has a tube with stopcock ahead from which the gas was collected. For preparation of this solution, first MEA was added to a suitable amount of distilled water and 30-35 wt% of alkanolamine was made ready into

which the H_2S gas from kipp's apparatus was bubbled through a 250 cm^3 gas bubbler. Since this reaction is exothermic, the MEA solution was kept in an ice bath for efficient absorbtion of the acidic gas and to prevent oxidiation of sulfide. The unabsorbed gas from the first solution was sent to the second containing 1M NaOH where it would react to form some products without escaping into the atmosphere. The experiments continued till the desired quantity of sulfide is obtained in the solution.

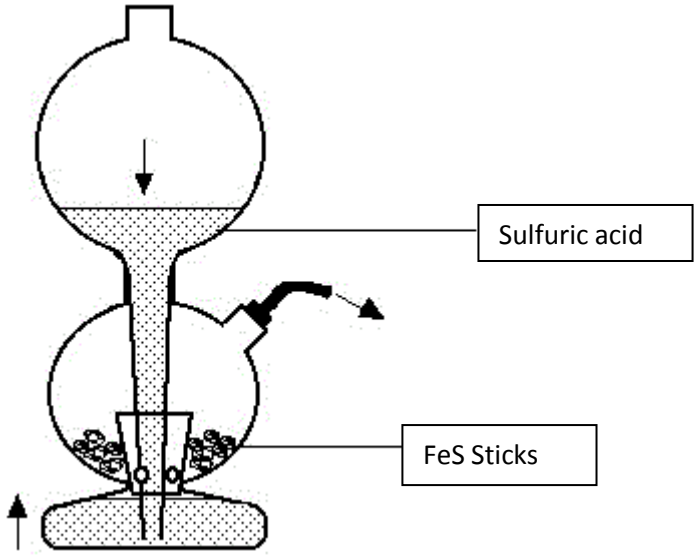


Figure 8. Kipp's Apparatus

3.3. Equipment

All the reactions were carried out in batch mode in a fully baffled mechanically agitated glass reactor of capacity 250 cm3 (6.5 cm i.d.). A 2.0 cm-diameter six-bladed glass disk turbine impeller with the provision of speed regulation, located at a height of 1.5 cm from the bottom, was used for stirring the reaction mixture. The reactor assembly was kept in a constant temperature water bath whose temperature could be controlled within ±1°C.

3.4. Experimental Methodology

The convention one variable at a time approach (OVAT) was followed where other variables where kept constant and only one varied and studied at a time. As in most scientific disciplines, chemists have historically followed the practice of changing one variable at a time (OVAT) during optimization. This method is useful to see the main effect of each variable on conversion and selectivity separately. The data obtained by this method, can be

used to get the order of reaction, optimize a simple reaction system, estimate kinetic parameters, to evaluate some thermodynamic parameters.

3.5. Experimental procedure

In a typical experimental run, 50 cm^3 of aqueous phase containing a known concentration of sulfide was charged into the reactor and kept well agitated until the steady state temperature was reached. Then 50 cm^3 of the organic phase containing measured amount of organic reactant (benzyl chloride), catalyst (PEG 400), and solvent (toluene), kept separately at the reaction temperature, was charged into the reactor. The reaction mixture was then agitated at a constant speed of stirring. Approximately 0.5 cm^3 of the organic layer was withdrawn at a regular time interval (1 hr) after stopping the agitation and allowing the phases to separate.

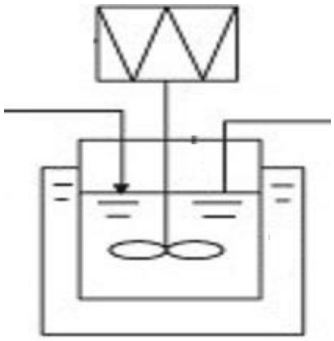


Figure 9. Batch reactor in water bath

3.6. ANALYSIS

3.6.1. Estimation of sulfide concentration

Hydrogen sulfide and soluble sulfides can be determined by oxidation with potassium iodate in an alkaline medium. 15 cm3 of standard (0.025M) potassium iodate solution was taken in a conical flask. 10 cm3 of sulfide solution containing about 2.5 mg of sulfide was then added to it followed by the addition 10 cm^3 of 10M sodium hydroxide solution. The mixture was boiled gently for about 10 minutes, cooled, and 5 cm^3 of KI solution and 20 cm^3 of 4M sulphuric acid solution were added to it. The liberated iodine was titrated, which was equivalent to the unused potassium iodate, with a standard 0.1M sodium thiosulfate in the usual manner. The potassium iodate in the alkaline medium oxidizes the sulfide to sulfate as given by the following reaction. For sulfide solution having sufficiently high sulfide concentration, suitable dilution was made before the estimation of sulfide by above mentioned procedure.

$$4\ IO^{3-} + 6\ OH^{-} + 3\ S^{2-} = 3\ SO_4^{2-} + 4\ I^{-} + 6H_2O$$

$$4 \text{ mole of } IO^{3-} \equiv 3 \text{ mole of } S^{2-}$$

3.6.2. Analysis of Organic Phase

All the samples from the organic phase were analyzed by gas–liquid chromatography (GLC) using a 2 m × 3 mm stainless steel column packed with 5% SE 30. A gas chromatograph (Chemito Model 8610 GC) interfaced with a data processor (Shimadzu C-R6A Chromatopac) was used for the analysis. The column temperature was programmed with an initial temperature of 150°C for 2 min, increased at a rate of 20 °C/min up to 300°C and maintained at 300°C for 4 min. Nitrogen was used as carrier gas at a pressure of 0.8 bar. An injector temperature of 250°C was used during the analysis. A flame ionization detector was used at a temperature of 300°C. The products were characterized by GLC. The composition of the samples being analyzed was calculated by direct comparison of the peak areas against a calibration curve. The term selectivity of the two products, DBS and BM, used in this study are defined as the fraction of BC converted to a particular product divided by the total conversion of BC.

%Selectivity of DBS = (moles of DBS formed/ moles of BC converted)*100%.

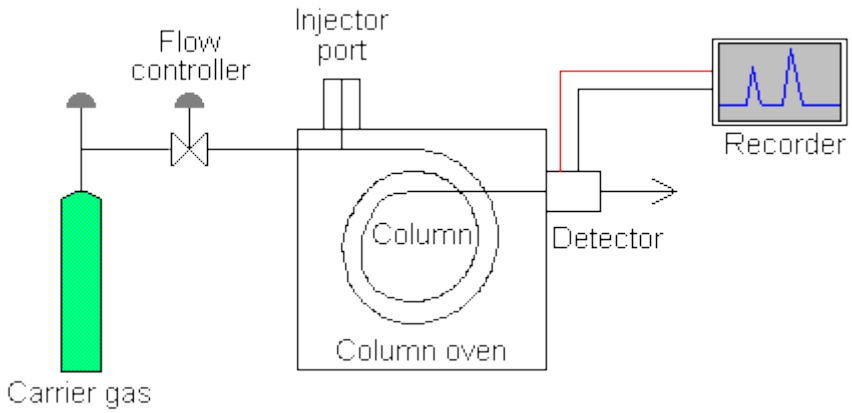


Figure 10. Working principle of Gas chromatography

CHAPTER 4

RESULTS & DISCUSSIONS

4.1. Effect of agitation speed

Two important steps are involved in the process of PTC, the mass transfer step and the intrinsic reaction in the organic phase or in this case the 3rd liquid phase. The kinetics of both these steps is interrelated and for getting a favourable PTC reaction, both the reaction rates have to be pretty fast. If the intrinsic reaction rate is faster than the transfer rate, then the overall rate is limited by the rate of mass transfer (PTC reaction of benzyl chloride and aqueous sodium cyanide) and this can be the other way too when rate is limited by the intrinsic reaction.

To study the proper kinetics of the reaction which would be helpful in kinetic modelling, the resistance of mass transfer has to be eliminated. The factors such as type of catalyst and inorganic anion contribute to these factors, but the agitation speed shows a more stronger effect on the transfer step, so the speed was varied from 400- 2000 rpm and the effect of it has been shown below in the figures.

At low speed, the conversion was also less, which signified the diffusion resistance was more that in turn gave low conversion values. At 1000 rpm the conversion was around 55% without catalyst which signified here reaction kinetics was limiting the reaction rate and the values were also doubled when catalyst was added and confirmed the same. The conversion range was from 65 to 92% when catalyst introduced at an agitation speed of 1500 rpm.

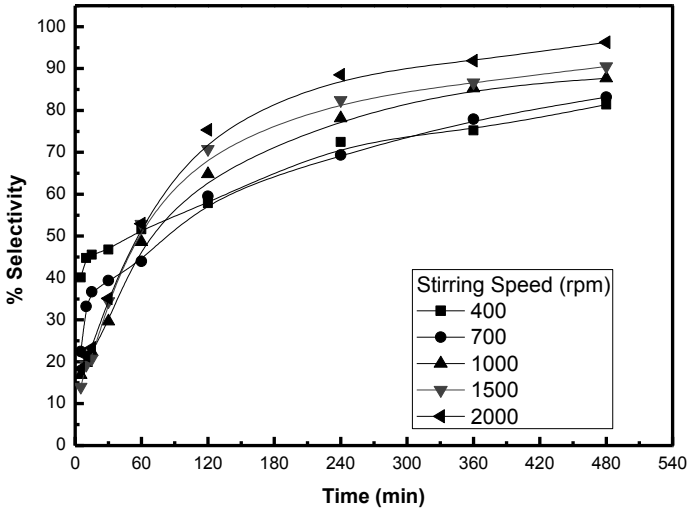


Figure 11. Effect of Agitation Speed on Conversion of BC

More than this range there was no significant increase in the values which explained the diffusion has been saturated at this stage. So increasing the speed could yield no more benefits. Therefore the further reaction runs were done at 1500rpm.

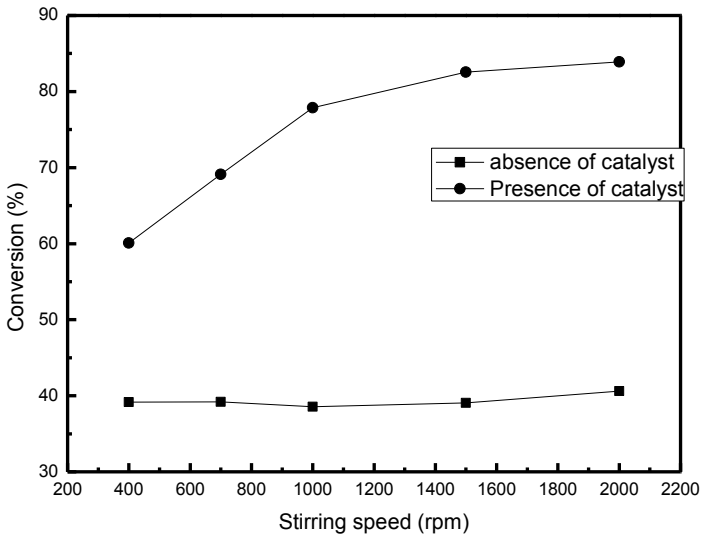


Figure 12. Comparison of conversion of BC in presence and absence of catalyst

4.2. Effect of catalyst loading

When the agitation rate increases to a critical value, the limiting step is dominated by the reaction within the catalyst-rich phase, so definitely the amount of catalyst would play an important role on the reaction rates. The conversion of BC and selectivity of DBS at various reaction times were studied by varying the catalyst concentration as it has been proved from the experimental values also that the mass transfer resistance is negligible at 1500rpm. The conversion was 65% for 0.05 kmol/m^3 of catalyst which showed that reactivity of a liquid catalyst is comparatively low and more catalyst is needed which is the only constraint compared to solid catalysts. The Catalyst loading was studied in the range of 0-0.15 kmol/m^3. But the conversion of the reactant BC started to get saturated after 0.10 kmol/m^3 and it was due to the maximum value of mass transfer of the reactants into the third liquid phase. But the selectivity was not showing the same trend; instead it increased with catalyst concentration.

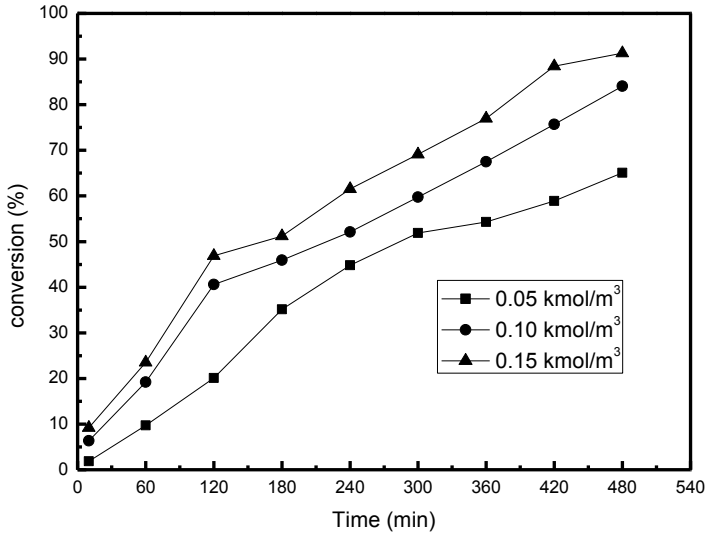


Figure 13. Effect of Catalyst Loading on conversion of BC

Mason et al. indicated that, when a reaction mixture forming a three-liquid system was reconstructed by separating the middle third liquid phase, the reaction rate dropped by over half, this was confirmed from the conversion % in presence and absence of catalyst.

4.3. Effect of reactant ratio

Ido et al. and Jin et al. conducted various experiments to conclude that reaction rate rapidly increased when the third liquid phase was formed and the stability of that phase also depends on the factors such as type and amount of aqueous reactant, reactant and product in the organic phase.

4.3.1. Effect of Initial sulfide concentration

The effect of initial sulfide concentration was studied keeping the MEA concentration fixed at 4.97kmol/m^3. The sulfide concentration was varied from 0.274–1.646 kmol/m^3. With fewer sulfide the conversion of BC was very low which can be attributed to the non-availability of reactant (sulfide) and the figure also proved that the conversion went up with the increase in concentration of the sulfide upto 80% when the concentration was 1.646 kmol/m^3. But considering the selectivity factor of DBS, it went up with the decrease in sulfide concentration. This effect was explained through the mechanisms in literature that although MEA does not take part in the reaction with benzyl chloride, it affects the equilibrium that results into two active anions, namely sulfide (S^{2-}) and hydrosulfide (HS^-) in the aqueous

phase. The concentration of sulfide ions relative to hydrosulfide ions in the aqueous phase increases with an increase in Initial sulfide: MEA ratio, which restricts the formation of BM.

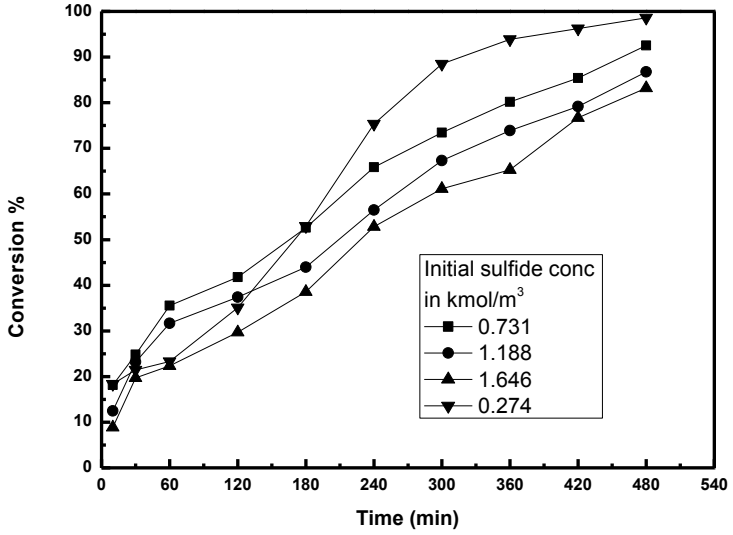


Figure 14. Effect of Initial sulfide Concentration on Selectivity of DBS

4.3.2. Effect of initial BC concentration

The effect of BC has been studied at different concentrations. Since pure BC has been used it will have a definite effect on the selectivity of the products. One can see that with increase in concentration the conversion value has went down which showed that limited quantity of the sulfide was the reason. So when concentration increased, there was not enough sulphide to promote the conversion.

But it showed that the full usage of the sulfide when the BC concentration was increased. Now considering the selectivity of the DBS, it went up with the concentration increase and reached up to 90%. As BM is formed first in the reaction and very fast compared to the formation of DBS, at low BC concentration BM becomes the most formed product reducing the selectivity of DBS. The contradictory results for each variation meant that the optimized value has to be chosen or else the amount of reactants would depend on the thing which we prefer more (conversion or selectivity).

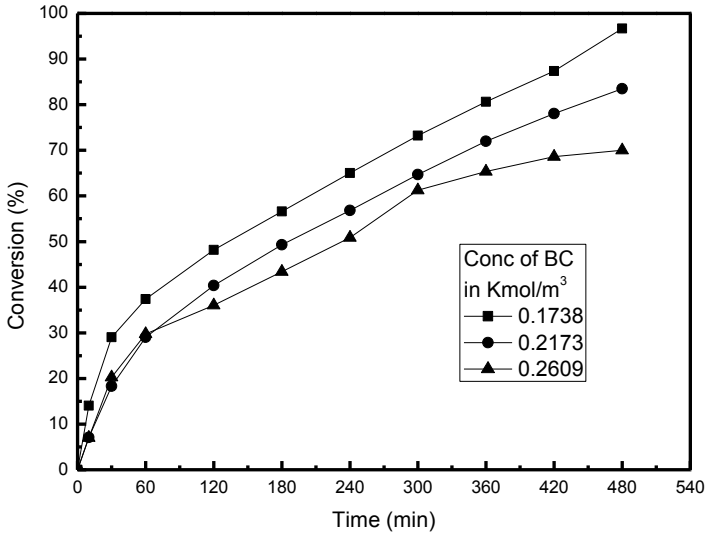


Figure 15. Effect of BC Concentration on Conversion of BC

4.4. Effect of Temperature

Increasing the reaction temperature accelerates the reaction rate. However, the catalyst existing in the third liquid phase as well as in the organic phase should still be maintained. Under strong base conditions in TLPTC, the catalyst and the active intermediate have the tendency to decompose at a high temperature, hence, a limiting reaction temperature should be kept in maintaining the third liquid phase. So the studies were conducted at 40, 50 and 60°C and the results revealed that the conversion increased with temperature as expected and the selectivity was maximum at 60°C. Maximum conversion was found to be 85% at 60°C, the temperature can be increased further, but the stability of the third liquid phase may be affected.

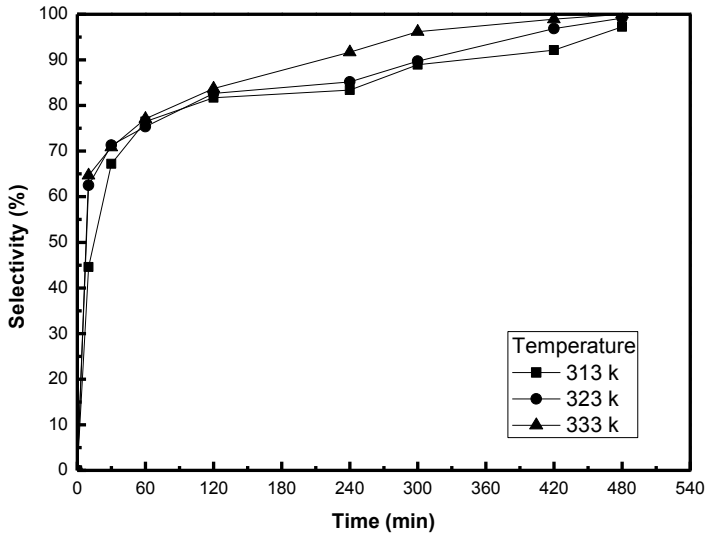


Figure 16. Effect of temperature on selectivity of DBS

PEG layer can exist till a temperature of 150°C, but it may be less for liquid PEG's and also the toluene boiling point is 110.6°C, so to see what maximum temperature can the reaction withstand, a study was conducted at 110°C which proved the above fact and the conversion reduced to 66% because of less amount of 3rd liquid phase, but this did not affect the selectivity of the products. DBS, the desired product was achieved more.

The above graph shows drastic decrease in activation energy compared to similar systems in the past which had activation energy around 45 kcal/mol. With PEG as catalyst there was a sufficient energy reduction which can be concluded as one of the requirements of green chemistry in designing a system.

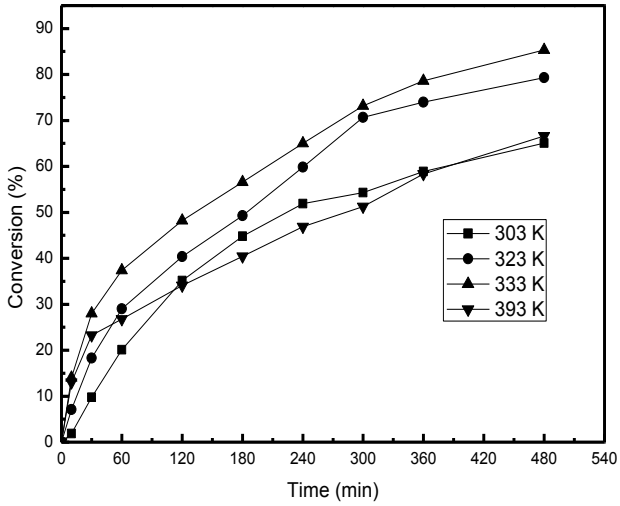


Figure 17. Effect of Temperature on selectivity of DBS

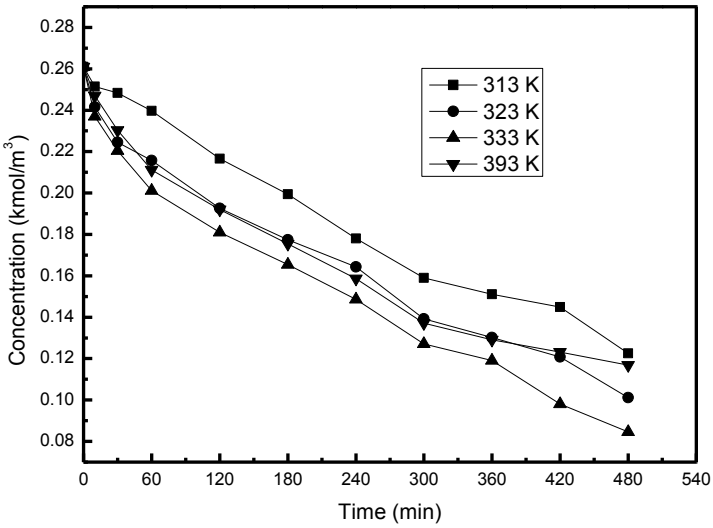


Figure 18. Plot of Concentration vs Time

Table 3: Variation of rate constant with temperature in presence of catalyst

Equation		**Y=a+b*x**	
R^2	0.98297	0.96264	0.95345
		Value	**Standard Error**
Concentration	Intercept	0.2541	0.00305
Concentration	Slope	-2.83316E-4	1.17815E-5
Concentration	Intercept	0.23931	0.00485
Concentration	Slope	-1.30572E-4	1.87676E-5
Concentration	Intercept	0.2337	0.00596
Concentration	Slope	-8.51284E-5	2.30424E-5

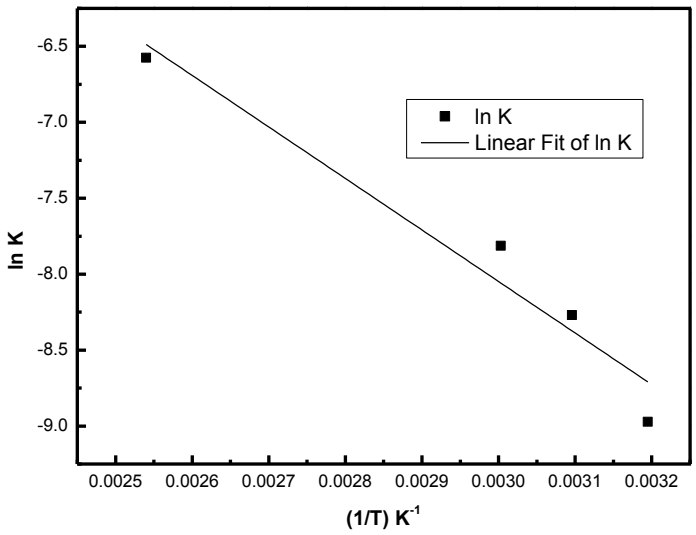


Figure 19. Plot of ln K Vs 1/T

Table 4: Activation energy and correlation factor in presence of catalyst

Equation		**Y=a+b*x**	
R^2	0.92731		
		Value	**Standard error**
ln K	Intercept	2.1281	1.6071
ln K	Slope	-3392.1176	541.2948

CHAPTER 5

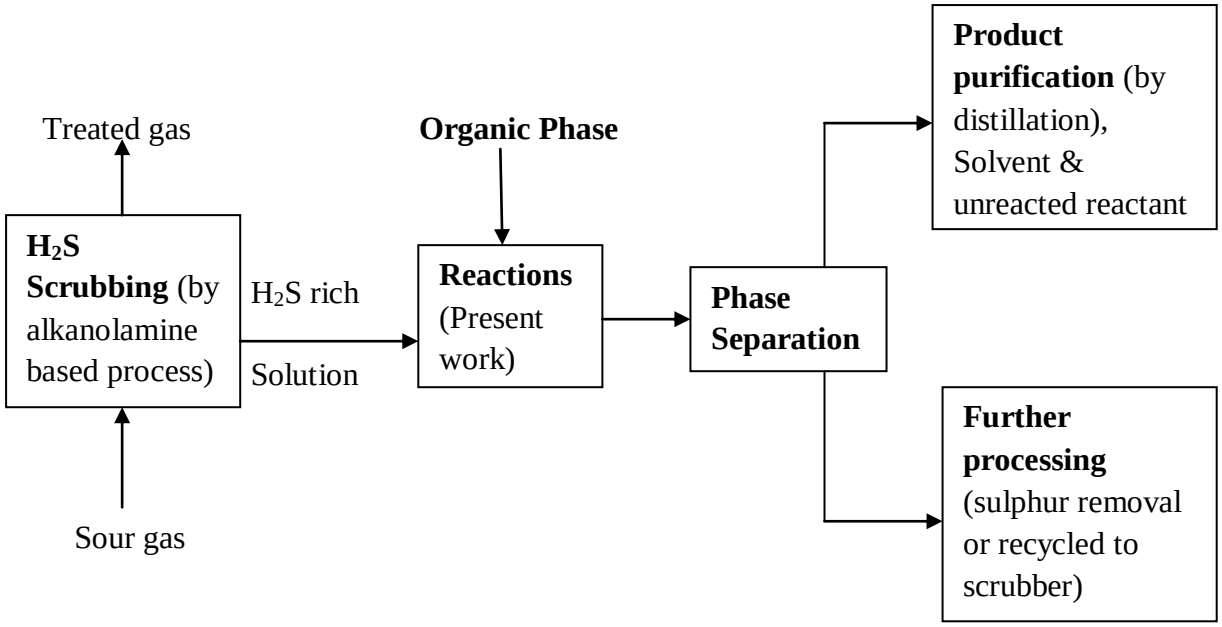
CONCLUSION & FUTURE SCOPE

Abstract

This chapter summarizes the concluding remarks from all the preceding chapters

5.1. Introduction

Since the removal of H_2S alkanolamines are well established and industrially practiced one, the present work deals with a detailed study and developing a state of the art process for the production of fine chemicals utilizing H_2S-rich alkanolamine in the batch mode. The strategy of the present process is schematically represented.



5.2. Summary & Conclusion from Chapter 4

The reaction of benzyl chloride with H_2S-rich aqueous monoethanolamine (MEA) in presence of a PTC (PEG 400) and solvent toluene leads to products (DBS and BM). One can selectively prepare either DBS or BM using the same reagents only by selecting proper operating conditions. The high MEA/H_2S mole ratio, high benzyl chloride concentration, and long reaction time lead to selective preparation of DBS. On the other hand, opposite trend was observed for BM. The reaction was found to be kinetically controlled with an apparent activation energy value of 10.2 kJ mol^{-1}. The process was determined to follow a complex mechanism involving the transfer of two active ion pairs ($Q^+S^{2-}Q^+$ and Q^+SH^-) from the aqueous phase to the organic phase and react with benzyl chloride to produce DBS and BM, respectively. The DBS is also formed by the reaction of BM and benzyl chloride.

The high MEA/H_2S mole ratio, high benzyl chloride concentration, and long reaction time lead to selective preparation of DBS. On the other hand, opposite trend was observed for BM. A maximum BC conversion of 100% and a maximum DBS selectivity of 97% were predicted under certain experimental conditions. Conditions for dual maximization of BC conversion (100%) and DBS selectivity (95.2%) were found as: temperature 333K, catalyst concentration 0.15 kmol/m^3, BC/sulfide mole ratio 2.83, MEA/sulfide mole ratio 3.7.

5.3. Scope for further work

This chapter shows the scope for works that can be proceeded on the same system for further improvement of the process based on the results of this experiment. And it tells what significant contributions can be made to phase transfer field by scaling up the process for industries.

5.3.1. Investigation of Mechanistic Pathways

There have been fewer studies on the mechanism of tri-phase systems. As this system had a good selectivity and conversion percentage, studying the mechanism would open up for new routes to synthesize different products. Aqueous phase can be analyzed to know the presence of several species (Cl^-, Br^-, HS^-, S^{2-}, Q^+ etc.) in it and then to quantify it to get better insight into the mechanistic pathway.

5.3.2. Finding out Effect of other Parameters

The effect of pH of H_2S-rich ammonia or alkanolamine solution needs to be explored. S^{2-}/HS^- ratio plays an important role in selectivity of benzyl mercaptan and benzyl sulfide which in turn depends on the pH of the alkaline solution. Effects of other anions as co-catalyst and addition of alkali (NaOH for example) that can influence the reaction rate and selectivity of desired products can also be tried.

In the present study, toluene has been used as a solvent in most of the cases because it is cheap. The physical properties of organic solvent play an important role on the PTC reaction, not only by influencing the intrinsic organic reaction but also by affecting the transport properties of PTC and active catalyst species (QSQ and QSH) (Yang et al., 2003). Other types of solvents like chlorobenzene, n-heptane, dichloromethane can be tried out.

5.3.3. Reusability of Catalyst

As one of the main positives of the 3 phase system is reusability, the factor can be studied which was not done in the above study. Studies can also be conducted with other kinds of PTC (solid PTC like 1,3,5-tris(benzyltriethylammonium bromide) benzene (TBTABB) (Balakrishnan et al., 2009a) or Polymer-bound PTC like polymer-anchored-2-benzyl-2-phenyl-1,3-bis(triethylmethylene ammonium chloride) (PABPBTAC).

5.3.4. Statistical Modelling & single pot synthesis using H_2S

Statistical models can be developed to find out kinetic parameters and the kinetic equation exactly matching our system for further optimization of the conditions. As this is a two step process which involves the absorption of H_2S and then followed by the synthesis of fine chemicals, it will be tough when done in an industry, so it's very essential to develop a single pot method or continuous process where H_2S can be allowed to react directly with aromatic compounds.

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